DEGRADATION PHENOMENA ON HISTORIC GLASS: NON-DESTRUCTIVE CHARACTERIZATION BY SYNCHROTRON RADIATION

Hannelore Roemich[1], Franco Zanini[2], Katrin Wittstadt[3],
Carola Mueller Weinitschke[4], Nicola Sodini[2]
[1]The Conservation Center, Institute of Fine Arts, New York University
14 East 78th Street, New York, NY 10075-1706, USA
FAX: +1 212 992-5851, hannelore.roemich@nyu.edu
[2]SYRMEP Group, Sincrotrone Trieste
S.S. 14 km 163, 5 in Area Science Park, 34012 Basovizza – Trieste, Italy
[3]Fraunhofer ISC, Bronnbach 28, 97877 Wertheim-Bronnbach, Germany
[4]Dombauverwaltung, Glasrestaurierung, Roncalliplatz 2, 50667 Koeln, Germany

ABSTRACT

Depending on their composition and the exposure environment, historic glasses develop degradation phenomena, ranging from thin hydrated surface layers up to complete cracking all through the sample. Characterizing the degradation pattern is important to select the most adequate conservation strategy.

Optical microscopy is the most frequently used non-destructive analysis methods to examine the surface of historic glass. Scanning electron microscopy (SEM) is applied to investigate the depth of damaged areas, although this requires the glass to be prepared as embedded cross sections and is thus limited to sacrificial samples. Computed X-ray tomography (CT) was adopted for detecting degradation layers on archaeological glasses by using a desktop tomography scanner. Limitations were encountered when the treatment of degraded glasses with organic polymers needed to be evaluated.

The highly coherent X-ray beam available at the SYRMEP bending magnet beamline at ELETTRA offers the possibility to investigate glasses by phase sensitive (PS) micro-tomography. Historic glasses from archaeological context and samples taken from naturally weathered stained glass windows were examined during a measurement campaign in 2007. The results demonstrate the potential of phase sensitive micro-CT to illustrate not only the corrosion patterns of glasses but also the conservation treatments. In one prominent example the consolidation of a cracked archaeological sample with Paraloid B72 could be followed. The visualization of the 3D-structure of fragile objects can be used to optimize conservation treatments.

INTRODUCTION

Glass is a material, which is fascinating and inspiring artists for more than four thousand years. Ancient glass objects belong to the masterpieces of arts and crafts in Europe. Stained glass windows are covering the period from the Middle Ages till contemporary creations. Glass pieces from different origins exhibit special degradation phenomena (Davison 2003, Tennent 1999, Roemich 2006). One of them is called “cracking” (Davison 2003). From far away and in transmitted light, the glass seems to be darker or iridescent. From closer look the pieces appear sugar-like. Crack patterns on corroded glasses are normally limited to the degraded surface area. In contrast, some stained glass windows of the 19th century as well as some archaeological vessel glasses predominantly from Roman times are cracked all the way through, such as a special type of yellow glass from Cologne Cathedral (see figures 1 and 2). The deterioration phenomenon is called “internal fractures” and looks similar to damaged toughened safety glass (Wittstadt & Mottner 2008, Müller 2003, Sloan 1999, Eggert 2006). The glasses suffer from visual light reflections at the fissures and mechanical instability.

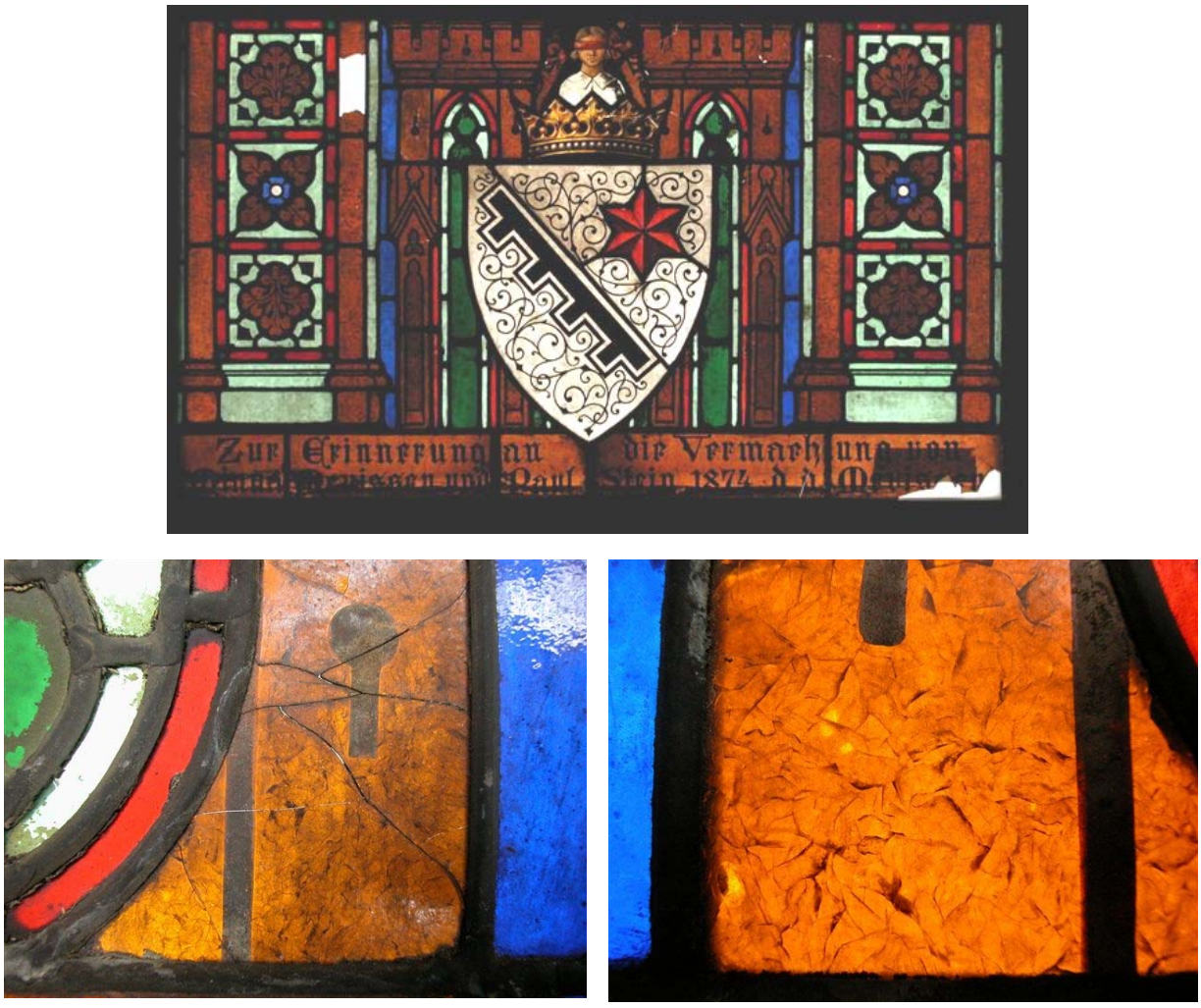

Figure 1: "Jesus-Sirach-Window", a panel and its details from a stained glass window in Cologne Cathedral (late 19th Century). The yellow glass pieces are heavily endangered by cracking due to internal fractures.

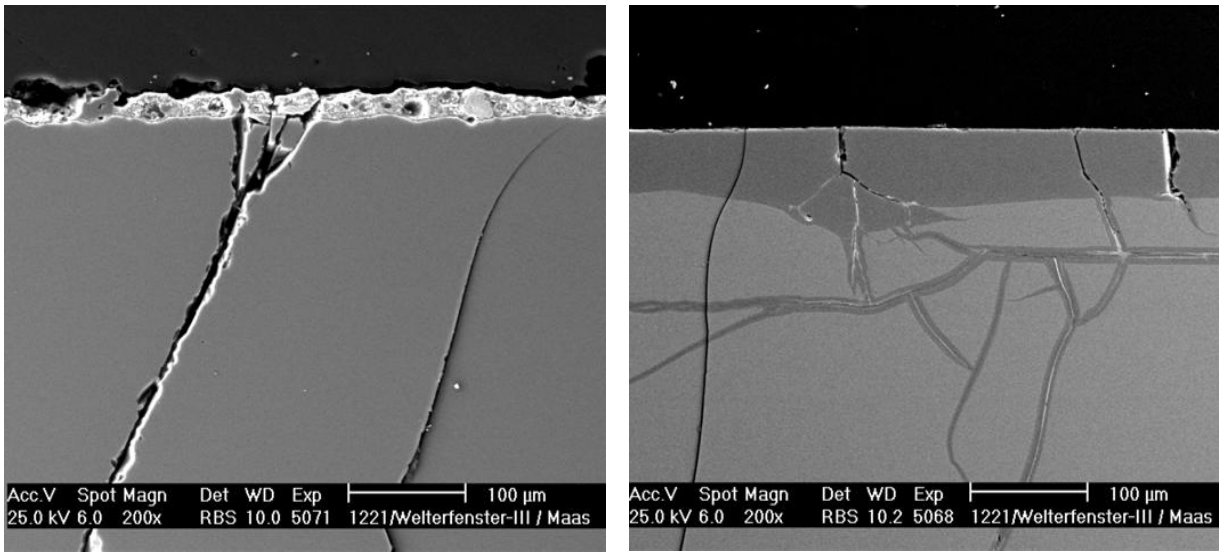

Figure 2: SEM cross sections (embedded and polished) of a sample of cracked stained glass (see figure 1); the size of the cracks are in the range of a few up to about 10 micrometer

The reason for glass degradation is connected to its composition and the interaction with the environment (Davison 2003, Tennent 1999, Roemich 2006). For the glasses from Cologne showing internal fractures, also an inappropriate manufacturing process (melting, tempering, and firing, after painting with trace lines) may have contributed to develop this form of degradation.

While the basic mechanism of glass degradation is known for long and described in the literature, the resulting reaction to form specific cracks still needs to be explored in detail. The size of the cracks (which are visible in transmitted light) can range from a few nanometers up to about 100 micrometers.

Ethics in conservation directs the responsible conservators to "preserve" the artworks as much as possible instead of just replacing parts of it. However, in the case of heavily cracked glass in windows there is no alternative and very often these pieces have to be replaced by new glass, which does not correspond to the overall idea of conservation. Archaeological vessel glasses with heavy cracks may never go on display and remain as a neglected resource in storage.

The challenge is to find a method to stabilize the glass and to keep it within the collection. The most obvious method to stabilize the cracks is by coating with a polymer. This treatment is only successful on the long term if the polymer penetrates in the cracks all the way through. However, a thick organic polymer as a coating on historic (uncleaned and corroded) glass would create problems due to aging and subsequent loss of adhesion. Therefore, the ideal concept is to achieve deep consolidation without leaving too much excess polymer on the surface.

Several organic and inorganic polymers are used for glass conservation (Davison 2003, Tennent 1999). Some of them have shown promising results for stabilizing cracked glass. However, the viscosity of the solution and the application technique (brush, pipette or immersion) has to be optimized. Any kind of improvement depends on the reliability of the detection technique. Normally, glass cracking is investigated by SEM by embedding a glass piece in a polymer and preparing a cross section. This is not possible if the polymer used for consolidation cannot be distinguished from the polymer used for embedding the sample. Several attempts to use tracers or markers in the polymer have failed. Furthermore, these experiments need to be carried out with valuable originals for which non-destructive techniques are required.

PHASE-CONTRAST TOMOGRAPHY AT ELETTRA SYNCHROTRON

Phase-Contrast Tomography

In conventional radiology the image formation relies on the X-ray absorption properties of the sample and can be expressed by means of geometrical optics. The image contrast is originated by a variation of density, composition or thickness of the sample and is based exclusively on the detection of amplitude variation of the transmitted X-rays. Information about the phase of X-rays is not taken into account. The main limitation of this technique is the poor inherent contrast in samples with low-Z composition: indeed this is the case for "soft matter" which is considered, in the common sense, as transparent to X-rays.

In contrast to absorption radiography, phase-contrast imaging techniques are based on the observation of the phase shifts produced by the object on the incoming wave. They are described by means of wave optics. Absorption and phase shifts are effects occurring to X-

rays crossing any kind of materials. Their relationship is considered in the definition of the material complex index of refraction n, that in the X-ray region slightly differs from unity: $n = 1 - \delta + i\beta$, where δ is related to the refractive properties and β determines the absorption. In the energy range between 15 and 25 keV, the phase shift term δ (of the order of 10^{-7}) can be up to 1000 times greater than the absorption term β (of the order of 10^{-10}). It is therefore possible to reveal phase effects even if the absorption is negligible (phase objects). The observation of the local variations in the optical path-length, determined by variations of δ, is related to Fresnel diffraction. In general, phase information can be accessed if the X-ray source has a high spatial coherence as in the case of synchrotron light sources (Snigirev et al 1995, Baruchel et al 2000, Cloetens et al 1997), such as ELETTRA.

Fraunhofer ISC in Germany had carried out research on archaeological glasses for which desktop micro-CT has been optimized as new non-destructive technique (Roemich et al 2005). The results were promising for detecting the corrosion patterns, but the material contrast between degraded glass and organic polymer (for treated pieces) was too low, so that treatments could not be evaluated. First attempts at ELETTRA by using the highly coherent X-ray beam were much more promising. The results from first experiments with phase-contrast microtomography were compared with the results from conventional analysis of identical samples and the results obtained by desktop-micro-tomography (Gerlach et al 2003, Gerlach et al 2006). The technique seemed very promising and encouraged further investigations. The challenge of the new measurement campaign was to explore the detection of cracks to find out which crack patterns and sizes can be visualized. By looking at untreated and treated samples the potential of the technique to detect conservation materials within cracks needed to be examined. Based on a new and non-destructive analytical method for consolidated cracked glasses, conservators could work in the future on the improvement of conservation methods.

The SYRMEP beamline with its optics based on a double-crystal Silicon (111) monochromator, working in an energy range between 8 keV and 35 keV seemed to be the right choice for the proposed samples. The beamline provided at a distance of about 20 m from the source, a monochromatic X-ray beam with a maximum area of (150 x 6) mm². The detector which was used is a 4008 (H) x 2672 (V) pixel CCD detector (pixel size = 4,5 μm, field of view 18 x 12 mm^2) in binning 2x2 configuration. A total number of 8 tomograms were recorded after setting the suitable parameters for the measurement to 27 keV energy, 720 rotations, and a distance between the sample and the detector of 66 cm. The question was whether treated and non-treated samples could be distinguished with this experimental set up (see figure 3). Therefore, some of the samples were measured non-treated and then they were treated while left in the exact position. In this way spectra related to the same position inside the sample could be provided in a non-invasive way, showing the difference between different phases of the treatment.

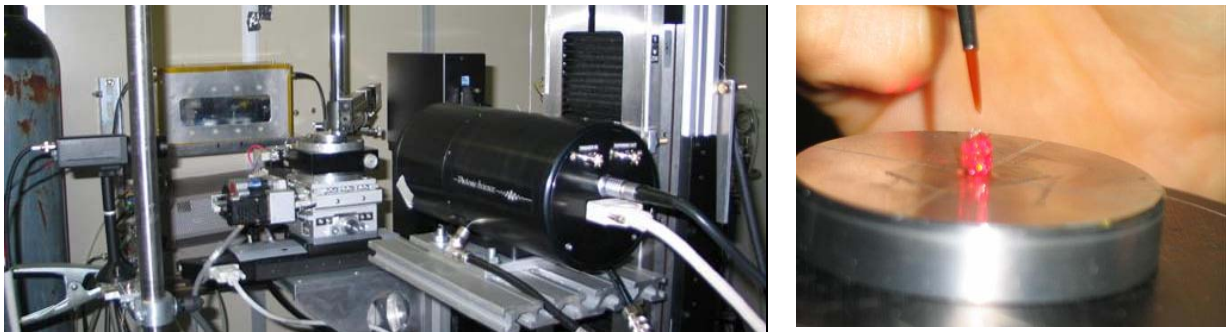

Figure 3: Positioning of the sample in the experimental hutch (left) and treatment of the sample with consolidant (right; sample appears red due to positioning laser)

SELECTION OF SAMPLES

In order to define the optimum measurement parameters, a reference sample was produced: a glass slide with a thick coating of polymer. Paraloid B72 was chosen as consolidant, since this is the most common treatment in glass conservation at present. It was applied by brush in toluene (5 or 10% solution).

Glass fragments from the 19th century window in Cologne Cathedral (see figure 1 and 2) were provided by Dombauhuette Koeln. The yellow glass pieces with internal fractures were measured without treatment and after various treatments: One of the yellow glass pieces was consolidated with 5% Paraloid B72 prior to measurement (sample 5). Another piece had been first measured without treatment (sample 7) and was heated in water afterwards for several hours to widen the cracks (then called sample 7-2). Later on the sample was consolidated "in situ" in the experimental hutch (see figure 3). An example for a yellow stained glass fragment is given in figure 4.

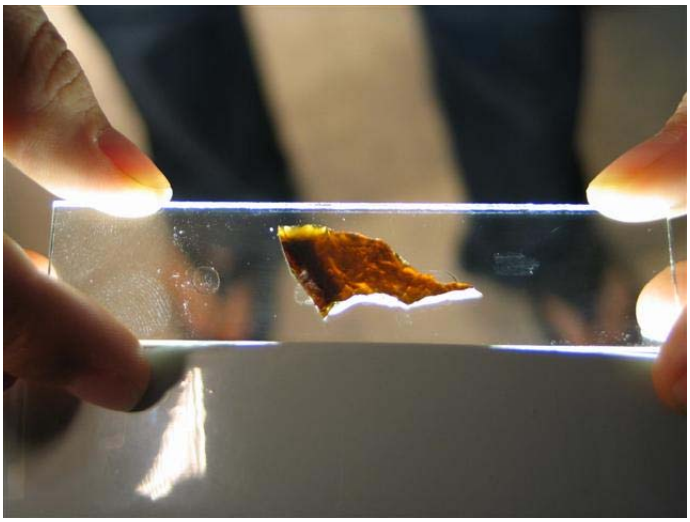

Figure 4: Yellow glass fragment from Cologne, being prepared for measurement

Archaeological glass fragments (provided through Fraunhofer ISC), with crack patterns running through the samples as well as crack patterns limited to the surface, have been selected to represent a broad variety of damage patterns. The overview pictures and the SEM cross sections are given in figures 5 and 6.

Sample RGM8 (figure 5) is a blue-brownish archaeological glass fragment from Germany. It exhibits the widest cracks, running all through the sample, which turns the glass opaque. According to SEM the width of cracks is up to 100 micrometer). Desktop CT images are available from a previous project (Roemich et al 2005).

LDA14 (figure 6) is a brownish opaque glass piece excavated in Germany. In the SEM image it shows a think corrosion layer consisting of thin lamellar sub-layers, covering the sound non-corroded bulk glass (thickness of corrosion crust varies between 100 and 300 micrometer). LDA13, again an archaeological fragment, shows an iridescent surface layer. In the SEM it becomes evident, that the layers are rather thin (up to 10 micrometer) with local pits. These samples had also been investigated by desktop CT in a previous project (Roemich et al 2006).

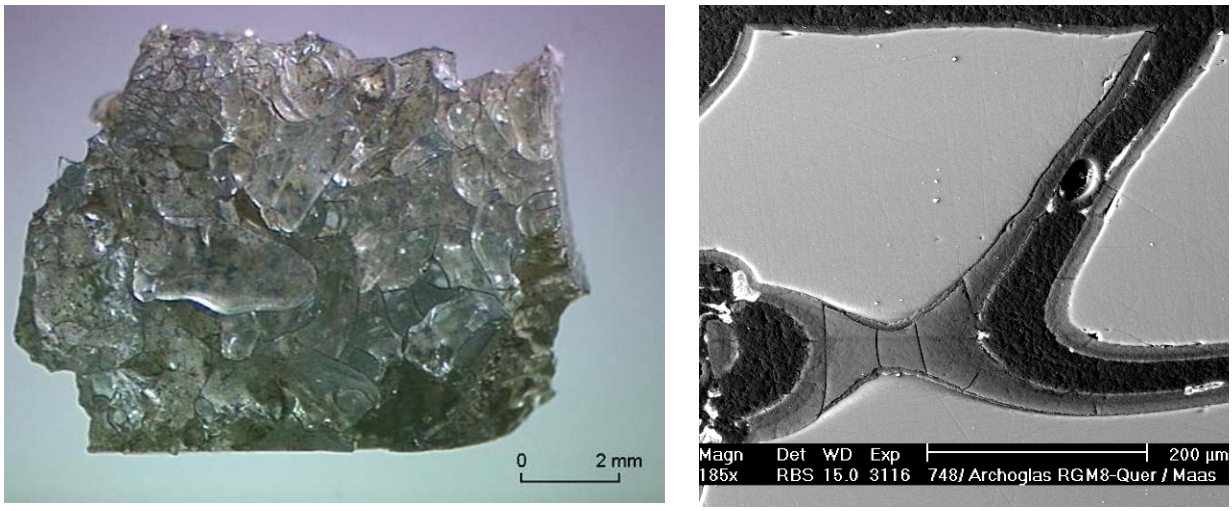

Figure 5: Archaeological glass fragment RGM8, overview and SEM cross section

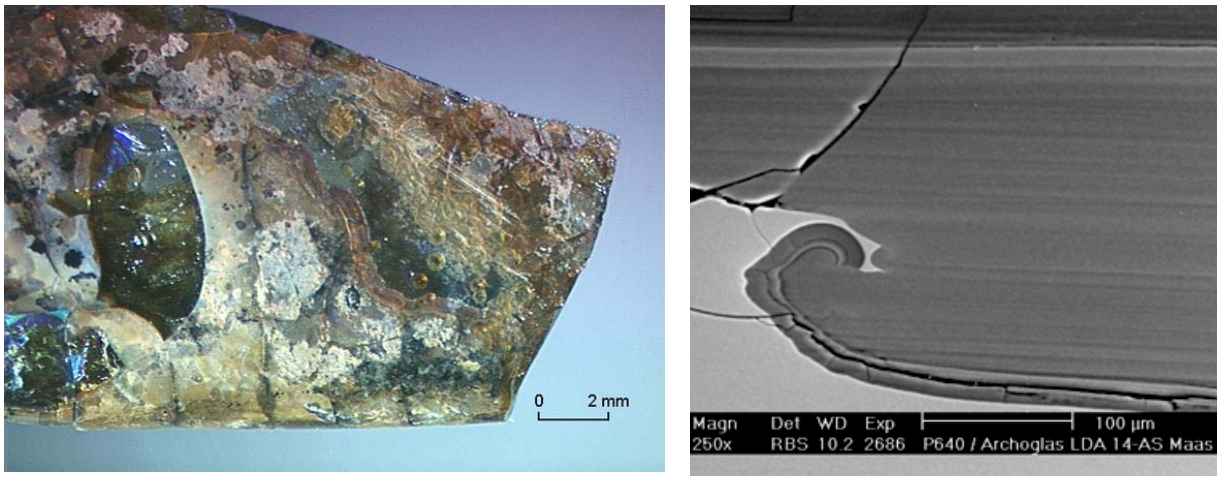

Figure 6: Archaeological glass fragment LDA14, overview and SEM cross section

RESULTS

Glass slide with thick coating of polymer: In the CT image the glass and the thick polymer layer could be distinguished easily, confirming the results from the previous measurement campaign. The experimental parameters were established based on these findings.

Sample 5 (yellow glass with visible cracks, treated with 5% polymer in Cologne): In the CT image the small cracks were barely visible. Probably there was no deep crack within the scanning volume of 3 mm^3.

Sample 7 (yellow glass with visible cracks, without treatment): the result was similar to sample 5 - only very narrow cracks can be detected as thin lines.

Sample 7-2: Sample 7, heated in water for about 12 hours and dried on a hot plate, in order to widen the cracks; the treatment has visually changed the sample: some cracks appear wider and the glass as such appears darker. Although the sample got visibly altered, the crack pattern in the CT appears still only as fine grey darker lines, where the dimension of the wider cracks is of the order of 5-10 micrometers. Smaller cracks cannot be seen with the experimental configuration we have chosen, characterized by a spatial resolution of about 5 micrometers in the phase-contrast regime.

Sample 7-2 poly: Sample 7-2, treated with 5% polymer, drying only a few minutes. After treatment with the polymer the crack pattern does not show significant differences in comparison with the untreated sample. Figure 7 shows a detail of a virtual slice of the treated sample, where some cracks can be detected.

RGM8: Already from SEM it was obvious that the cracks in this sample are one order of magnitude wider than in samples 5 and 7 from Cologne. In the CT the structure of channels is clearly visible. Some cracks are running all the way through the sample, others are penetrating only partly. Some cracks are filled with corrosion products (which can be seen and also detected by analysis of the grey value).

Sample RGM8 was treated with 5% polymer for consolidation. After drying during the night, the new CT scan showed small but detectable changes of the crack structure. The consolidation was repeated with 5% polymer (drying time: about an hour) in the experimental hutch by keeping the same position in the beam. The second treatment has filled most of the cracks, completely or partially. A subtraction of the images (before and after polymer treatment) was difficult, because the sample was slightly moved and thus the files do not fit perfectly for mathematical subtraction. However, the analysis of the grey values in the cracks (filled with polymer or corrosion products) was more successful for the difference between the first and second polymer application: the comparison of CT images on the exact same spot allows the estimation how far the solution was penetrating. In the single slices the polymer can be seen on some outside surfaces and also in the cracks (see figure 8).

The single virtual slices of scans can be reconstructed as 3D image of the sample, which is an ideal way to visualize the crack structure (figure 9).

LDA14, LDA13-2: The corroded archaeological glass fragments have developed a corrosion layer (variation in structure and thickness), which can be detected in the CT. The results confirm the findings from SEM, although the thickness of the single lamina (detectable in SEM) is below the spatial resolution of the synchrotron experimental setup. The added value is the third dimension in the CT images, providing information about the homogeneity of the layers (SEM provides only one single cross section, which might not be representative).

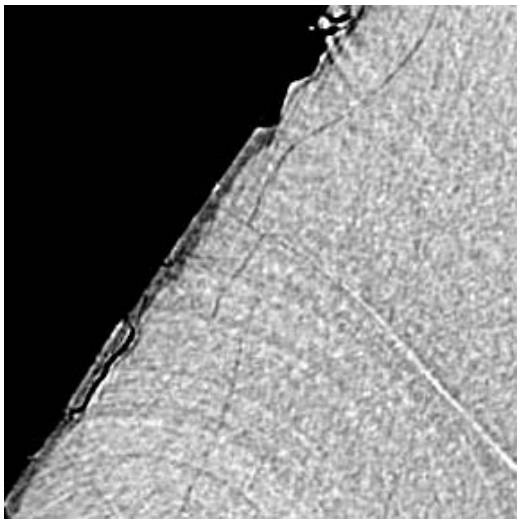

Figure 7: CT image, virtual slice of sample 7-2 after treatment (image size = 1.3 x 1.3 mm2)

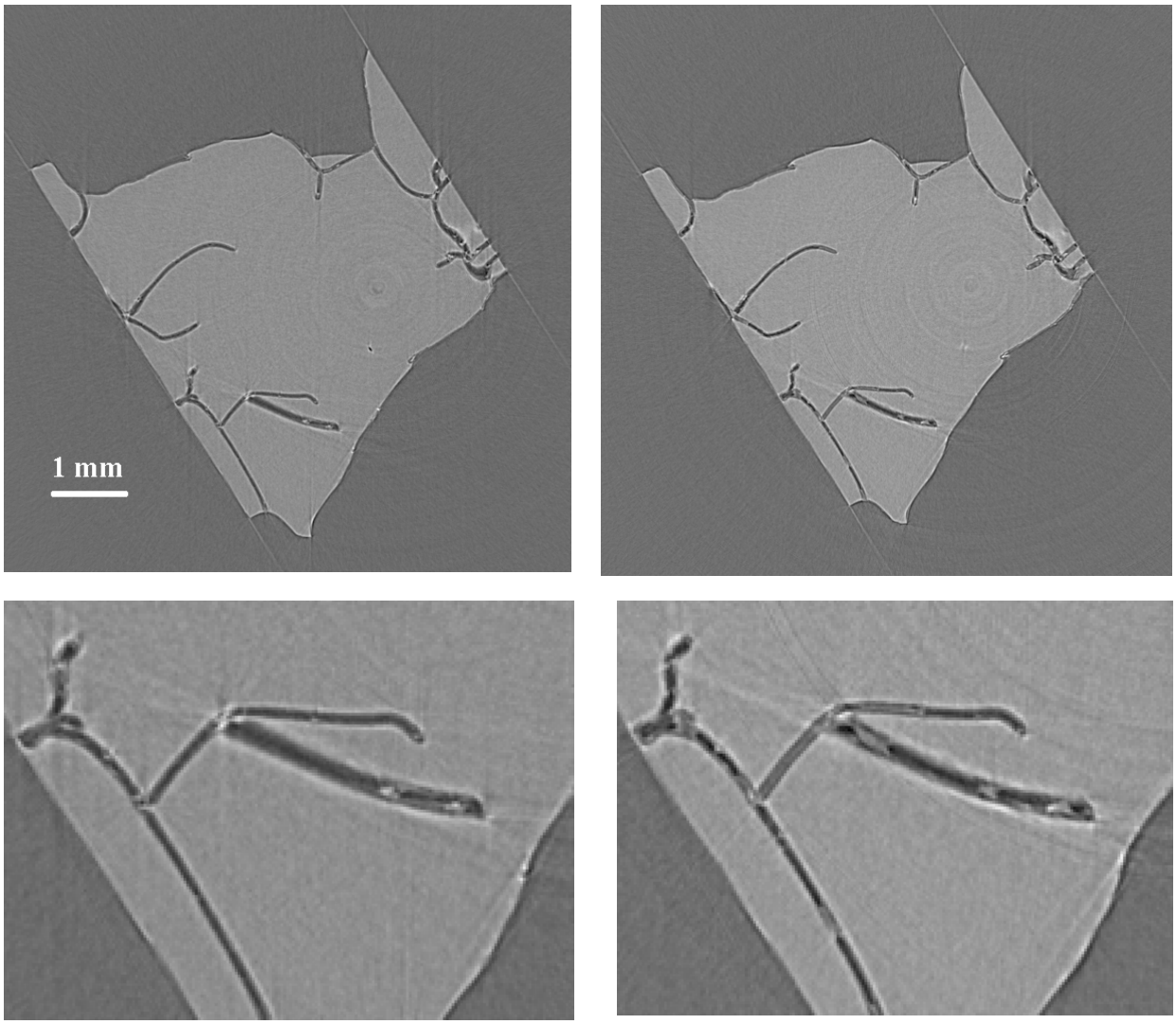

Figure 8: CT image, virtual slice of sample RGM8 after a first application of 5% polymer (left) and the same slice of the same sample after another application of polymer (right); overview images are in the top row and details are given below. The images show a gradual fill of the consolidant in the cracks.

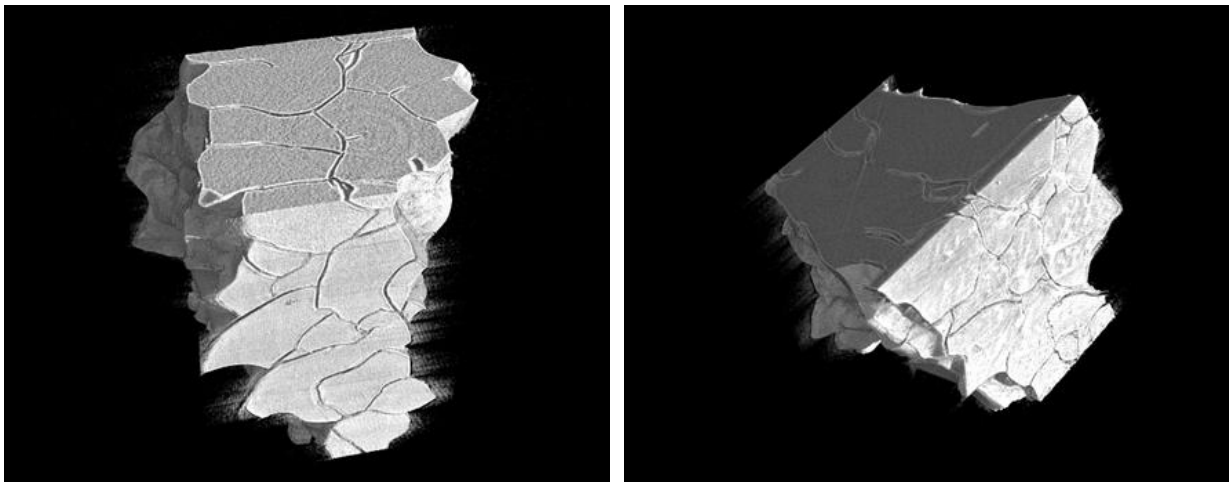

Figure 9: 3-D reconstruction of CT scans of sample RGM8 (untreated); the total volume is about 3 mm3

CONCLUSION

The detection of consolidants in degraded glasses by non-destructive techniques is crucial for further improvements of conservation treatments. Phase-contrast computed tomography, a technique based on the observation of the phase shifts produced by the object in a highly coherent X-ray beam, has been identified as a promising analytical tool for corroded glasses.

For this study glass samples exhibiting internal fractures have been selected and their crack pattern has been investigated before and after treatment with a consolidant. The yellow glass samples from a stained glass window in Cologne look heavily damaged, as visible in transmitted light. This is due to refraction from a discontinuity surface in a transparent medium, which is a macroscopic effect even if the crack dimension is in the order of micrometers or less. This is confirmed by the SEM analysis of cross sections, which shows that cracks are thinner than 10 micrometer. CT images showed only very thin lines representing the cracks, even after attempts to widen the cracks by heating.

In the analysis of archaeological samples with broader cracks (such as RGB8), the spatial resolution of the X-ray detector was compatible with the lateral dimension of the cracks, which was of the order of 40 micrometers, while the dimensions of the slices (of the order of 1 cm^2) was compatible with the statistics required by the analysis. The difference between empty and filled cracks, which could not be detected by means of conventional X-ray microtomography, were successfully visualized by phase-contrast CT in this experiment.

In future investigations, a detector with a higher resolution could allow the analysis of samples with smaller cracks, but at the expense of the field of view of the system. An X-ray detector with a pixel size of 1 μm, for example, has been used so far for the reconstruction of slices of 1 mm^2, which is not enough for a satisfactory description of the consolidation procedure.

Further research on samples with cracks smaller than 10 micrometer will thus concentrate on the development of digital subtraction microtomography. In this technique two data sets are collected, one just above the X-ray absorption edge of the element to be imaged, and the other just below the same absorption edge. The contrast in the difference between the two data sets is almost entirely due to the presence of the element of interest. Silver could be an ideal candidate, having a K-edge at 25.5 keV, i.e. very close to the photon energy of 25 keV, which is ideal for the composition and size of this kind of samples. We plan to use silver nitrate as

contrast solution, since it has already been successfully used for digital subtraction tomography applied to the analysis of nanoleakage in dental reconstruction (Prisco et al 2003). Phase-contrast digital subtraction tomography needs a monochromatic, tunable and coherent X-ray source, so a synchrotron radiation source is again the only possible choice.

ACKNOWLEDGEMENT
The authors acknowledge the possibility to examine historic glass samples at ELETTRA (Proposal No. 2006707, Crack patterns in stained glass: research for improved conservation). The archaeological glass fragments have been investigated at Fraunhofer ISC in a previous project (supported by the Deutsche Bundesstiftung Umwelt, reference number 15851-45).

1. **BIBLIOGRAPHY**
Baruchel, J., Cloetens, P., Härtwig, J., Ludwig, W., Mancini, L., Pernot, P., Schlenker, M. (2000): J. Synchrotron Rad., 7, 196-201
2. Cloetens, P., Pateyron-Salomé, M., Buffière, J. Y., Peix, G., Baruchel, J., Peyrin, F., Schlenker, M. (1997): J. Appl. Phys., 81, 5878-5885
3. Davison S., (2003): Conservation and restoration of glass, Butterworth-Heinemann, Oxford
4. Eggert, G. (2006): To whom the crack tell. A closer look at craquelure in glass and glaze. Studies in Conservation 51, 69-51
5. Gerlach, S., Römich, H., Lopez, E., Zanini, F., Mancini, L., Rigon, L. (2006): Phase contrast microtomography for archaeological glasses. In "COST Action G8 – Non-destructive testing and analysis of museum objects", Fraunhofer IRB Verlag, Stuttgart, Germany, 147-151
6. Gerlach, S, Römich, H., Lopez, E., Zanini, F., Mancini, L., Rigon, L (2003): Phase contrast microtomography for archaeological glasses. ELETTRA Highlights, 80-83
7. Prisco D., De Santis, R., Rengo, S., Ambrosio, L., Zanini, F. (2003): A Novel Non-destructive Technique to Investigate Interface Leakage using the Synchrotron Coherent X-ray Beam, 81 General Session of the International Association of Dental Research, Göteborg (Sweden)
8. Roemich, H.; Lopez, E.; Mees, F.; Jacobs, P.; Cornelis, E.; Van Dyck, D.; Domenech Carbo, T. (2005): Microfocus X-ray computed tomography (mCT) for archaeological glasses. In: Cultural Heritage Conservation and Environmental Impact Assessment by Non-Destructive Testing and Micro-Analysis, Taylor & Francis Group, London, 37-47
9. Roemich, H.: Glass and Ceramics. In: "Conservation Science – Heritage Materials" (eds E. May and M. Jones), the Royal Society of Chemistry Publishing, Cambridge, UK (2006)
10. Snigirev, A., Snigireva, I., Kohn, V., Kuznetsov, S., Schelokov, I. (1995): Rev. Sci. Instrum., 66, 5486-5492
11. Tennent N. H. (1999): The conservation of glass and ceramics, James & James, London
12. Wittstadt, K., Mottner, P. (2008): Internal fractures on glass objects. Glass Science and Art Conservation Congress, Valencia, submitted to the Journal of Cultural Heritage, special issue
13. Müller, W. (2003): Neues zur Konservierung von Glasmalereien um 1900. Teil 2: Fallbeispiele für Schadensbilder und Restaurierungsvorschläge. Restauro 2, 100-109
14. Sloan, J.L (1999): American Opalescent window glass. Composition and deterioration issues. 12th Triennial meeting, Lyon, reprints Vol.2, 803-808

Back to Top